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16. ABSTRACT

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Gas chromatography-mass spectrometry is a widely used technique for the identification of organic chemicals in water. This paper describes the gas chromatograph-mass spectrometer system, the preparation and separation of samples, the selection of ionizing processes, the integration of a computerized identification system, and the interpretation of mass spectra to identify organic chemicals.

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Water Quality Measurement

THE MODERN ANALYTICAL TECHNIQUES

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Chapter 1

ORGANIC WATER POLLUTANT ANALYSIS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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Integral to setting and enforcing water-quality criteria, determining the fate and effects of water pollutants, and developing optimum control measures is the ability to identify specific organic compounds. The contribution of the chemical analyst to environmental pollution control is further emphasized by the results of an analysis of industrial wastes illustrated in Table 1. As the table shows, twice as many compounds were identified by chemical analysis in the plant effluent as were predicted by the discharger based on knowledge of products, raw materials, and processes.

The identification technique selected by the analyst must be highly specific, because thousands of compounds must be considered, and highly sensitive, because organic compounds can cause problems at very low concentrations [for example, some are toxic to aquatic organisms at concentrations below 10 micrograms per liter (μg/l)]. Currently, the method that best meets these requirements for organic

*Dr. Webb is deceased.

Table 1. Comparison of Compounds Reported by Discharger with Compounds Identified by EPA in an Industrial Effluent

Products or raw materials reported	Compounds identified	
Propylene	All xylenes[a]	1,5-Cyclooctadiene
Ethylene	Isopropylbenzene	Styrene[a]
Butadiene	*o*-Ethyltoluene	*o*-Methylstyrene[a]
Butane	Diacetone alcohol	Indan[a]
Octane	2-Butoxyethanol	β-Methylstyrene
Ethylene glycol	Indene[a]	Dimethylfuran isomer
Ethylene oxide	*n*-Pentadecane	1-Methyl indene[a]
Polyglycols	3-Methylindene	Acetophenone
Ammonia	*n*-Hexadecane	α-Terpineol
Raw gas	Naphthalene[a]	Both methyl naphthalene isomers[a]
Ethane	Benzyl alcohol	Both methyl naphthalene isomers[a]
Refinery gases	Ethylnapthalene	α-Methylbenzyl alcohol
Refinery C_2 Stream	2,6-Dimethylnaphthalene[a]	Phenol [a]
	2,6-Dimethylnaphthalene[a]	Methylethylnaphthalene
Refinery C_3 Stream	Cresol isomer	Acenaphthene
	Acenaphthalene	Methylbiphenyl isomer
Propane	Fluorene	Two phthalate diesters
Hydroformer gas	3,3-Diphenylpropanol	
Platformer gas	3,3-Diphenylpropanol	

[a]Identification confirmed with a standard.

pollutants in water is gas chromatography-mass spectrometry (GC-MS). Any compound that can be gas chromatographed without decomposition can be analyzed by GC-MS.

The earliest applications of GC-MS analysis in water pollution studies dealt with industrial effluents containing milligram-per-liter (part per million) amounts of materials [1]. With recent improvements in sample concentration techniques, the application of direct GC interfacing to a mass spectrometer, and the use of a computer for machine control and data processing, however, materials present at only a few micrograms per liter (part per billion) can be readily identified. Analyses at part-per-trillion concentrations are often made as well. Along with advancements in sensitivity, GC-MS has undergone a marked improvement in identifying components of an environmental sample. As a consequence of improved sensitivities, better chromatographic columns, and computerized spectral matching, today's systems can identify many more compounds in water samples in 1 day than could have been identified in 6 months by early systems.

One reason for the widespread use of GC-MS in water pollution analysis is its ability to do two jobs well. It is unsurpassed as a method for surveying and identifying a broad range of organics in water with moderate sensitivity. Moreover, it can be used to find minute traces of specific individual compounds through the use of specialized techniques such as single-ion monitoring (SIM).

The most common type of water pollution analysis in the Environmental Protection Agency GC-MS laboratories is the general organic survey of industrial effluents, although increased emphasis has been placed recently on the survey of organics in drinking waters. In addition, GC-MS is applied to the analysis of taste and odor problems; the confirmation of pesticide residues; the identification of "volatile" organics such as chloroform, vinyl chloride, and bromoform; the analysis of sewage and landfall leachate; the preparation of baseline studies before major construction; and the analysis of water and tissue samples from fish kills.

The first use of MS in a water-pollution study involved the identification by John Teasley of the Athens Federal Water Pollution

Control Administration (now EPA) Laboratory of a pesticide derivative causing a fish kill in Charleston Harbor in 1966 [2]. The next year the laboratory purchased a GC-MS instrument exclusively for analysis of water samples. Each succeeding year has seen more laboratories, both here and abroad, begin to use GC-MS for pollutant analysis. Within the U.S. Environmental Protection Agency alone, for example, there are now 50 GC-MS systems.

Each year has also seen the number of compounds identified increase in direct correlation with the amount of effort devoted to this research. Recently, several international efforts have been initiated to prepare complete lists, accessible by computer, of all compounds identified in air, water, and biota. For each compound, information would be given on concentrations, geographical locations, frequency of occurrence, and toxicity.

As an example of typical materials identified by GC-MS, the following compounds were found three to five times in different industrial effluent surveys in the Southeastern United States from 1971 to 1973:

Acenapthene	Palmitic acid
Dehydroabietic acid	Pentachlorophenol
Dibenzofuran	Pentadecane
Dodecane	Phenol
2-Ethyl-1-hexanol	α-Terpineol
1-Methyl naphthalene	Tridecane
Naphthalene	Undecane
o-Nitrotoluene	

Among the materials commonly found in various waters are normal hydrocarbons containing up to 26 carbons, aromatic hydrocarbons, haloforms and chlorinated solvents, phthalate plasticizers, chlorinated ethers, phenols, pesticides, and various fatty acids.

I. GC-MS OPERATION

The gas chromatograph may be thought of as a specialized inlet for the mass spectrometer. In the most common mode of operation, a

compound enters the mass spectrometer and is exposed to an electron beam. This high-energy electron beam dislodges one or more electrons from the neutral molecule and leaves a charged, often unstable, molecular ion that usually fragments into several charged species of lower atomic weights. By electrical or magnetic methods, the MS then scans or "filters" all the ions so that they arrive at the detector in reasonably discrete groups. The groups consist of all the ions having the same atomic mass-to-charge ratio, that is, all singly charged ions of mass 43, all singly charged ions of mass 44, etc. The detector measures the current produced by the ions of each group and sends the signal to an appropriate recording and storage device, which in modern mass spectrometers is a computer. The computer can be instructed to operate a plotter or cathode-ray tube and display the MS scan in graphical form, such as Fig. 1. The x axis lists mass-to-charge values (m/e) rather than mass values. Usually the two are the same,

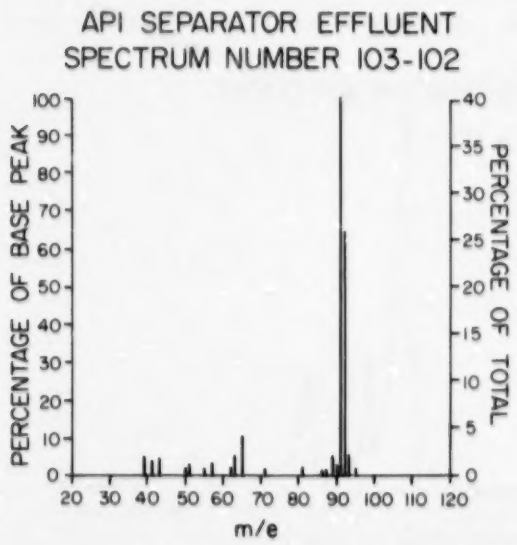

Figure 1. Typical bar graph representation of the mass spectrum of toluene.

but some molecules form ions of double charge and give a m/e signal that is half their actual mass. The most intense mass peak in a spectrum, called the *base peak*, is arbitrarily assigned an amplitude of 100. All the other fragment peaks are normalized to the base peak and their intensities are plotted as percentages of the base peak. This method of presenting the data helps make the spectra of identical compounds taken on different mass spectrometers directly comparable. This comparability feature, coupled with the fact that most individual organic compounds have unique fragmentation patterns, and hence unique spectra, makes MS a powerful identification tool.

In GC-MS, the mass spectrometer, usually under computer control, measures and stores a complete mass spectrum every 1 to 5 sec. As the run proceeds, the total ion current produced during each scan can be continuously plotted to provide a chromatogram like any other GC detector. At the end of the run, a reconstructed gas chromatogram (Fig. 2) is plotted. In this plot, the largest total ion current observed in the run is given a value of 100 and the other values are plotted relative to it. The x axis shows the spectrum number where

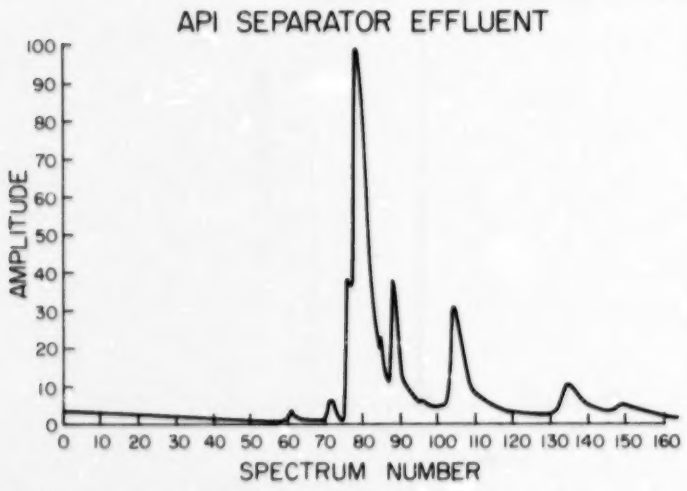

Figure 2. Reconstructed gas chromatogram.

each current was observed. Figure 1 is the spectrum representing the difference between spectrum 103 of Fig. 2 and the baseline spectrum 102.

II. SAMPLE PREPARATION

Before any GC-MS identification can be made, the sample must be obtained from the environment and processed so that it is suitable for gas chromatography and thus for GC-MS.

Occasionally, sample preparation is not required. Direct aqueous injection of 1 or 2 μl is sometimes used with samples suspected of having one or more components present at part-per-million levels [3].

The more common course, however, is to remove and concentrate the organics from the water by some form of extraction or sorption. The three most useful methods have been solvent extraction, sorption on solids (accumulators), and the most recent addition to the sampling arsenal, volatile organics analysis (VOA). Each of these methods has its limitations, and each month's technical literature contains papers describing improvements, criticisms, and modifications of sampling methods and devices.

The application of the VOA technique, developed largely by Bellar and Lichtenberg [4,5], was the key to the discovery of the widespread presence of chloroform, bromoform, and other bromine-chlorine-containing species in our drinking waters. Traces of these materials have probably been present in drinking waters since water-treatment systems adopted chlorination for bacterial disinfection. They had not been detected previously because the common extraction methods involve solvents (often chloroform itself) whose elution period in GC analysis overwhelms the area of the chromatogram where these materi usually occur.

With VOA, a small (5-500 ml) sample of water is placed in a closed system and a stream of inert gas is passed through the water and then led through a trop of porous polymer before venting to the room. The volatile organics that are stripped from the water are absorbed on the polymer. The unique feature of the polymers used as

traps is that they do not absorb water vapor. The trap is then placed in the heated inlet of a GC and the hot carrier gas desorbs the organics into the GC column.

The VOA technique has allowed quantitative detection of microgram-per-liter (ppb) amounts of materials that are less than 2% soluble in water and boil below about 150°C. A large number of aromatic and aliphatic hydrocarbons and their chlorine, bromine, and iodine derivatives fit these criteria. Although VOA is not quantitative for highly water soluble materials at low concentrations, enough of these materials can be isolated prior to analysis to allow qualitative identification by using a 500-ml or larger sample and heating it during the gas-purging step.

An alternate method for isolating low-molecular-weight alcohols, simple ketones, amines, volatile acids, ethers, and other similar materials is to collect the first 25-30 ml of distillate from a 500-ml sample, redistill the 25-ml portion, and collect the first milliliter. The analysis is by direct aqueous injection.

Many of the gas-chromatographable materials present in water are also solvent extractable, a factor that is a key to their isolation. Obtaining a representative sample is one of the major problems in extraction, as well as other preparation techniques, however. Lake and river waters are not homogeneous, and industrial effluents change with time. To solve this problem, some investigators prefer to take subsamples from various locations and at different times and to combine them for analysis. Moreover, many chemists avoid filtering the sample because the colloidal and suspended particulates frequently have organics sorbed on their surfaces.

The volume of the sample collected is usually 1 to 4 liters. Compounds present in a 1-liter sample at concentrations of 2 µg/l or greater will generally give good quality spectra when processed by extraction, concentration, and GC-MS techniques. Larger samples are required, however, if the analysis is for compounds present at lower concentrations. For example, 20-liter samples of municipal sewage have been processed with an apparent detection limit of 0.1 µg/l based

on an internal standard added to the extract before concentration. As a practical matter, however, multiple samples larger than about 4 liters are usually not processed by extraction because of the excessive labor and handling involved.

Because samples may have to be transported or stored for a considerable time before analysis, cooling or freezing is usually used to stop biological action and prevent chemical changes. The addition of strong acid as a preservative is not recommended because it degrades sensitive compounds such as geosmin and 2-methyl isoborneol (taste- and odor-causing compounds). Glass sample containers are usually packed in ice at the collection site and are refrigerated in the laboratory at about 4°C.

A typical isolation procedure is to extract a liter sample of water with two or three 50- to 100-ml portions of solvent. The combined extracts are evaporated to 1 ml or less for GC analysis.

The two most popular solvents are methylene chloride and chloroform. Methylene chloride has a much lower inhalation toxicity than chloroform and thus is safer to use. Other solvents in common use are petroleum ether, hexane (also 15% diethyl ether in hexane), diethyl ether, and carbon tetrachloride. Petroleum ether and hexane are so nonpolar that they do not effectively extract polar materials such as fatty acids and phenols. Therefore, some investigators prefer to do a first extraction with one of these solvents and then isolate the more polar materials with a second extraction using chloroform or methylene chloride. We do not recommend ether (except in very small quantities for diazomethane methylations) because of its flammability, the danger of explosion from peroxide impurities, and the presence of additives. Various preservatives are added to ether to inhibit peroxide formation but are not usually listed on the container label. For example, one peroxide inhibitor identified by GC-MS and later confirmed by the manufacturer was 2,6-ditertiarybutyl-p-cresol. This compound was recognized as an artifact because it also occurred in the blank. Finally, in solvent comparison studies, ether was found to be only half as effective as chloroform in extracting a paper-mill

effluent. In any case, the solvent should be as pure as possible; pesticide grade (distilled in glass) material is recommended.

Extraction is affected by the hydrogen ion concentration (pH) of the sample. Organic acids are ionized salts in basic solution and will not extract into organic solvents. Therefore, samples containing fatty acids (municipal sewage) or phenols (forest runoff) are best extracted at a pH < 3 to ensure maximum covalent character. Similarly, basic materials are best extracted at high pH. A complete, but somewhat involved, procedure for these "solubility class" preparations are given by Braus et al [6]. Many variations in procedure are possible and each problem requires an individual judgment.

After a sample is extracted, a little water may remain dissolved in the solvent. The analyst can either dry the extract before concentration or concentrate the solvent directly. With chloroform extracts, better recoveries of the dissolved organics occur when the solution is evaporated directly than when drying by sodium sulfate or when glass wool is used [7]. If drying with sodium sulfate is essential, then it should first be heated to 500°C for 2 hr to remove organic impurities, usually phthalate esters.

The best method for concentrating the organic extract is distillation with a Kuderna-Danish (K-D) evaporator (Fig. 3). The bottom and middle flasks are filled to about half the nominal flask capacity. Boiling chips are added and the whole assembly is placed on a boiling-water bath or a steam bath in a hood. The water level should be maintained just below the bottom joint and steam should bathe the rounded bottom of the middle falsk. Distillation is usually continued until about 1 ml of liquid remains in the concentrator tube; the whole assembly is then removed and allowed to cool. As the liquid drains from the condenser, it rinses the residue from the walls of the middle flask. The final volume is about 5 ml.

The calibrated concentrator tube is removed and placed in a beaker of warm water (<70°) and the volume reduced to any desired amount, usually 1 ml, by directing a stream of clean dry air or other gas over the surface. A procedure that results in better recoveries

Figure 3. Kuderna-Danish evaporator.

in this final evaporation step is the use of the mini-K-D evaporator (Fig. 4) [7].

Sometimes a sample needs to be taken over a period of several days to adequately reflect what is happening in the study area. In other cases a very large (hundreds to thousands of liters) sample is required to achieve the desired sensitivity. These sampling problems have been most often resolved using the carbon absorption method (CAM). The sampler is often a glass cylinder, 7 × 45 cm, packed with both a coarse and a fine carbon. A prefilter may be used to prevent clogging by suspended solids. After the sample has been collected (1 day to several weeks), the carbon is removed and dried--usually in a 40°C oven, but occasionally by freeze drying. The entire sample is then

Figure 4. Micro-Snyder column evaporator (mini-Kuderna-Danish).

extracted with several liters of chloroform in a special glass Soxhlet extractor. The chloroform extract contains most of the compounds amenable to GC, but for other purposes, the chloroform extraction is sometimes followed by one with alcohol and this portion analyzed separately. A long list of weaknesses can be given for the CAM--ranging from the fact that no two batches of carbon are ever exactly alike to the problems of incomplete desorption with chloroform--but it has been the most often used method for long-term sampling.

Numerous other methods have been proposed to replace solvent extraction and carbon absorption. In our experience, freeze concentration and steam distillation are inferior to extraction. Polyure-

thane foams are now being used to extract polychlorinated biphenyls directly from water [8]. These foams, coated lightly with GC phases such as DC-200, also extract organochlorine pesticides [9]. Our tests, however, show that neither material is effective for extracting dissolved oil, phenols, or terpenes [7]. Organic resins, particularly the monionic XAD series, are very effective for a broad range of materials but are not universally applicable [7,10]. For example, they are very poor at removing gasoline-type n-paraffins, amino acids, low-molecular-weight alcohols, ketones, and short-chain fatty acids. However, there is the possibility of using combinations of resins of different types to overcome these problems. In general, the resins' uniformity from batch to batch, their low background levels, and their complete desorption characteristics make them the most likely replacements for carbon. Two other unique, and worthwhile, approaches for overcoming sampling problems for GC-MS are described by Grob [11-13], and Mieure and Dietrich [14].

When extracts of water are analyzed by GC for pesticides or other specific organic compounds, the extract usually must be "cleaned up" to remove interferences. The most widely used technique is Florisil or silica gel column chromatography, sometimes in combination with acetonitrile partitioning. Thin-layer chromatography, preparative GC, and liquid chromatography are used less frequently. Fortunately, because the mass spectrum of a compound is much more definitive than its GC retention time, extracts for GC-MS analysis generally need not be cleaned up, particularly when solubility-class separation has been used during sample extraction.

If preliminary GC runs show that cleanup of the extract is necessary, the concentrated extract is chromatographed on activated Florisil. In the original technique [15], increments of solvent containing increasing proportions of ethyl ether in petroleum ether are used to elute fractions containing increasingly polar organics. We prefer the use of methylene chloride as an eluant, as described in an analysis report on dieldrin in a textile-plant effluent [16].

III. SAMPLE SEPARATION

As another approach, after solubility separation of the crude extract, the neutral fraction may be further separated on a silica gel column. Successive elution with isoctane, benzene, and 1:1 chloroform:methanol separates organics into aliphatic, aromatic, and oxygenated organic fractions, respectively [17].

Thin-layer chromatography (TLC) is sometimes used as a preliminary separation technique for GC-MS analysis. Samples of industrial and municipal effluents contain so many components that direct TLC of extracts usually gives only unresolved streaks. In a few cases, intermediate cleanup by TLC is useful, resulting in the separation of bands of compounds of the same type. This type of sample cleanup has been used in the identification of pesticide metabolites by GC-MS [18].

Liquid chromatography (LC) has occasionally been used as a preliminary separation tool for GC-MS. The LC solvent is usually removed and the residue derivatized to produce volatile components that may be analyzed by GC-MS. Recently, the LC has been directly interfaced with the MS to produce an analysis system that is expected to prove useful in the future.

Many compounds are not volatile enough to be vaporized without decomposition. Such polar compounds as carbohydrates, amino acids, sulfonic acids, and nucleic acids are not directly gas chromatographable. In addition, steroids, carboxylic acids, and phenols can be directly chromatographed in their free form, but require special columns and techniques not readily available. Phenols "tail" on most GC columns, steroids elute too slowly, and only recently have columns become available for the efficient separation of free long-chain carboxylic acids. These problems are solved through the use of derivatization reagents now available for all these classes of compounds. Methyl derivatives, in the form of methyl esters of carboxylic acids or methyl ethers of phenols, and trimethylsilyl (TMS) derivatives of carbohydrates, steroids, phenols, amines, and carboxylic acids are the most common.

For gas chromatography, glass and metal columns of 1/8-in (3 mm) inside diameter are inexpensive and readily available. Most mass spectrometers will accept them. The analyst must be careful not to inject the large amounts of solvents (5-10 µl) traditionally used because this raises the gas pressure past acceptable limits in most mass spectrometers. Most GC-MS systems will accept injections of 1-2 µl. For routine surveys, packed columns are most often used.

Although capillary columns offer the ultimate in peak resolution, they are tedious to prepare inhouse and expensive to buy commercially. In spite of the problems involved, they are being used more and more commonly. In particular, glass capillary columns are finding widespread use in GC-MS in Europe, and at least a dozen laboratories in this country are preparing them for their own use. For samples as complex as those usually obtained from environmental sources, the capillary column is rapidly becoming an expected part of the GC-MS equipment.

Many liquid phases are available to the chromatographer. The two most useful in our work are SE-30 (nonpolar) and Carbowax-20M terminated with terephthalic acid (polar).

Temperature-programmed GC is nearly always used for GC-MS analysis. A medium program rate of 4°C/min is common. Frequently, the program is extended to the upper limit recommended for the liquid phase. At the resulting high temperatures, considerable bleed occurs with many columns. For example, MS fragments at m/e 73, 147, and 221 resulting from dimethyl silicones appear when the usually stable silicone columns, such as SE-30, are overheated. The program should therefore be terminated short of these high temperatures.

Helium is the usual carrier gas for GC-MS systems (except for the chemical ionization technique discussed in Chapter 3). The carrier-gas flow rate is often more dependent on the molecular separator that interfaces the GC column and the MS than on the column itself. With glass frit or jet separators, the flow through the column can easily be 15-20 ml/min. The normal flow for capillary columns is 1-2 ml/min, and they are often connected directly to the MS inlet without the use of a separator.

When it is necessary to remove part of the carrier gas to keep the mass spectrometer ion source pressure below 10^{-5} torr, some form of separator must be used. There are several kinds; all have the common objective of fractionating the effluent gas from the chromatograph so efficiently that a maximum amount of sample contaminated with a minimal amount of carrier gas is introduced to the mass spectrometer. McFadden [19] has discussed both the theory and the design for all common separators.

Most commonly used for the analysis of organic pollutants of water is the glass jet separator [20] (Fig. 5), which consists of two sections of glass tubing that end in capillaries of different diameters. The tubing is aligned within an evacuated region so as to have a 0.5- to 1.5-mm gap between the ends of the capillaries. The gas mixture from the chromatograph leaves the narrower capillary as a jet under turbulent flow condition. The gas jet passes through a very short region where it is exposed to vacuum and then is collected by the larger capillary and introduced into the mass spectrometer ion source.

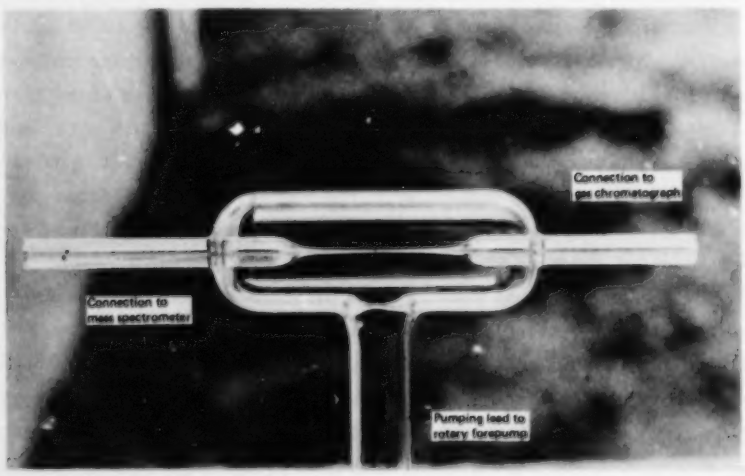

Figure 5. Glass jet separator (From W. H. McFadden, *Techniques of Combined Gas Chromatography/Mass Spectrometry*, 1973, reproduced with permission of John Wiley and Sons, Inc.)

During the passage through the evacuated region, lighter molecules are preferentially pumped away so that the gas introduced into the mass spectrometer is richer in heavier molecules. Because separation is based on diffusion, higher molecular weight materials are concentrated more efficiently than low ones. This type of separator is preferred for most environmental applications because it has shown less tendency to fractionate or decompose thermally labile materials than other common separators. The jet separator has one serious limitation: the narrower capillary tends to plug when column bleed becomes excessive.

The next most common type of separator [21] for environmental use is the frit separator. In this separator (Fig. 6), the effluent gas from the chromatograph passes through a tube, part of which is made by fritting together glass beads of less than 1-mm diameter. This tube is surrounded by a continuously evacuated envelope. When the frit has been made properly, most of the carrier gas will pass through the interstices of the frit and be removed as the sample passes through the tube into the mass spectrometer. This separator exposes a large area of glass frit to the chromatographic effluent; it is essential that polar sites of the frit be deactivated to prevent absorption and catalytic cracking of thermally sensitive samples.

Other types of separators have been used by many gas chromatography-mass spectrometry laboratories but are not widely used in environmental work. These include the variable path separator and the various types

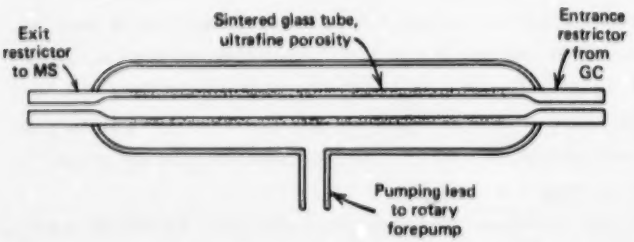

Figure 6. Glass frit separator, usually called a *Watson-Biemann separator*. (From W. H. McFadden, *Techniques of Combined Gas Chromatography/Mass Spectrometry*, 1973, reproduced with permission of John Wiley and Sons, Inc.)

of diaphragm separators. The variable-path separator of Brunée et al [22], permits the user to control effusion rate, and hence optimize it for any given separation.

The membrane separator [23], which is based on permeation through a semipermeable membrane, consists of a very thin silicone rubber diaphragm at the GC-MS interconnection. The organic sample rapidly penetrates the rubber and enters the mass spectrometer; whereas the carrier gas, which penetrates the membrane much less efficiently, passes to the atmosphere.

The metal-diaphragm separator requires high-purity hydrogen as the carrier gas. The diaphragm consists of a heated palladium-silver alloy that will pass the hydrogen but will not pass any of the sample components [24]. This device permits total removal of carrier gas without physical removal of sample; however, catalytic reduction and dehydrogenation of the sample are potential problems.

The separator from a gas chromatograph is the most common inlet system for environmental mass spectrometry, but by no means the only one. An inlet system such as that shown in Fig. 7 will permit introduction of either high-pressure gas mixtures or of liquid samples directly into an expansion volume, from which they are allowed to effuse into the ion source of a mass spectrometer. Numerous modifications of this basic design, as well as techniques to better use it, are discussed by Hamming and Foster [25]. This inlet type is the conventional method of introducing mass calibration standards such as perfluorotributylamine (FC-43) or perfluorokerosine (PFK).

Another common introduction system for a mass spectrometer is the heated probe, which is useful for both solid and liquid samples. When vapor pressures are not excessive, this inlet permits a sample as small as 1 ng of material to be introduced directly into the ion source of a mass spectrometer. Temperature of the probe can be programmed from subambient to 400°C. This capability permits crude fractionation of many mixtures.

In preparing a sewage treatment plant effluent for GC-MS analysis, an analyst at the Athens Laboratory noted that a blue solid separated

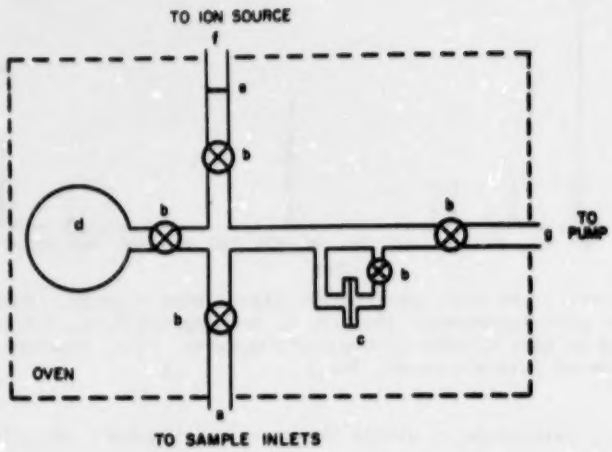

Figure 7. Schematic components of a multiple-purpose inlet system. a, Large-diameter heated port to gas, liquid, and solid inlets; b, suitable isolation valves; c, micromanometer or other pressure measuring device; d, sample reservoir expansion volume; e, capillary or gold leak; f, heated tube to ion source; and g, large-diameter tubing to diffusion and mechanical vacuum pumps. (From M. C. Hamming and N. G. Foster, *Interpretation of Mass Spectra of Organic Compounds*, 1972, reproduced with permission of Academic Press, Inc.)

from the organic fraction. He isolated this solid, which was introduced into a mass spectrometer by a direct insertion probe. The spectrum obtained (Fig. 8) was that of copper phthalocyanine, which was traced to the effluent from a paint manufacturer.

Several types of interconnections, the most noteworthy of which are presented by Lovins [26], Scott et al [27], McLafferty and coworkers [28], and Horning et al [29], have been used between liquid chromatographs and mass spectrometers. Lovins et al described a system that automatically isolated a liquid-chromatographic peak of interest on a solid probe, evaporated the solvent from it, and introduced the residue to the mass spectrometer. Scott et al allowed the effluent of the chromatograph to be trapped on a continuously moving wire that passed into the ion source region through a series of vacuum locks. Solvent was evaporated during the transfer and the solute was

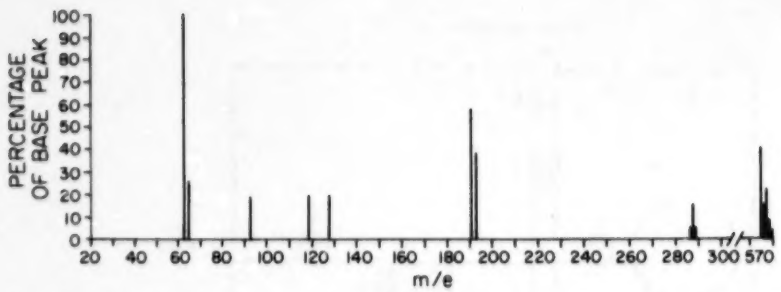

Figure 8. Direct-probe mass spectrum of suspect blue pigment, identified as copper phthalocyanine. (From M. M. Hamming and N. G. Foster, *Interpretation of Mass Spectra of Organic Compounds*, 1972, reproduced with permission of Academic Press, Inc.)

flash-heated to volatilize it within the mass spectrometer. McLafferty and his co-workers sampled a small fraction of the effluent from the chromatographic peaks. Horning and his associates ionized the effluent from a liquid chromatograph in air by means of a ^{63}Ni emitter. The plasma that was formed was sampled through a small orifice, and the ions formed were then separated in a mass analyzer to give an atmospheric pressure ionization spectrum. At this time, none of these techniques has been used for environmental analysis and will not be considered further in this chapter.

IV. ION FORMATION AND SELECTION

When a sample is first introduced into the mass spectrometer ion source by means of any of these inlet systems except that of Horning, it consists of neutral molecules. Before a mass spectrum can be obtained, it is necessary to ionize some of these molecules. This ionization step can produce either negative or positive ions and can take place by any of several different ionizing processes. In environmental analyses, positive ions that are produced by either electron-impact (EI) ionization or chemical ionization (CI) are typically used; however, recent work by Hunt and his associates [30] suggests that negative chemical ionization spectra may be used more widely in the future.

The ionization process involves insertion (negative ion) or removal (positive ion) of one or more electrons in the molecule. Primary ionization mechanisms may be grouped into several classifications as shown in Table 2. Of these mechanisms, reactions 1 and 2 are the most important for analytical electron-impact mass spectrometry; reactions 3 through 6 are important in analytical chemical ionization mass spectrometry. (See Chap. 3 by John G. Dorsey in this book.) Negative ionization techniques as represented by reactions 7 and 8 are not widely used in pollutant analysis.

Electron-impact ionization generally takes place in a small ionizing region between an electron source and an anode. This area is under vacuum with typical pressures between 0.1 and 10 torr. A schematic view of an electron impact source is given in Fig. 9. Electrons emitted by the hot filament (cathode) pass through the ionizing region normal to the path of the incoming sample. The ions formed are expelled from the ionizer and introduced to the focusing lens by the field between the repeller and focus electrodes. The ion beam is focused for optimum sensitivity.

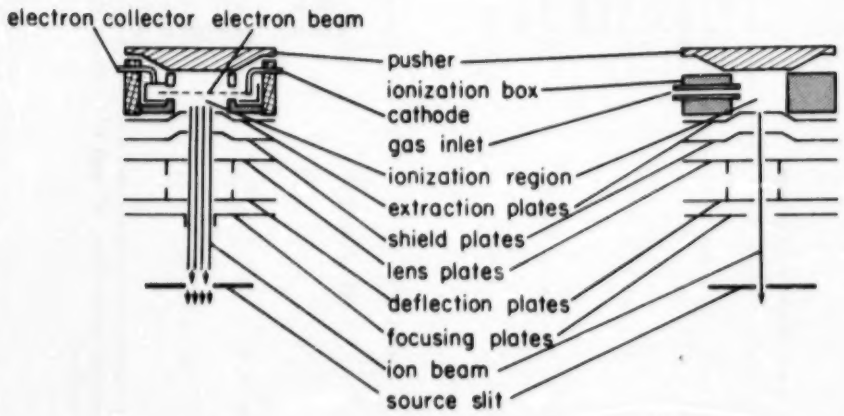

Figure 9. Schematic views of a typical electron-impact source. (Courtesy of Varian MAT.)

Table 2. Ionization Mechanisms

Reaction	Type	Typical example
1. $M + e^- \rightarrow M^+ + 2e^-$	Electron detachment	$CH_4 + e^- \rightarrow CH_4^+ + 2e^-$
2. $M + e^- \rightarrow M^+ + M^\circ + 2e^-$	Dissociative electron detachment	$CHCl_3 + e^- \rightarrow CHCl_2^+ + Cl + 2e^-$
3. $M + R^+ \rightarrow (M - 1)^+ + RH^\circ$	Hydride abstraction	$C_{10}H_{22} + C_2H_5^+ \rightarrow C_{10}H_{21}^+ + C_2H_6$
4. $M + R^+ \rightarrow MH^+ + (R-H)^\circ$	Proton transfer	$(C_8H_{17}OOC)_2C_6H_4 + CH_5^+ \rightarrow [H(C_8H_{17}OOC)_2C_6H_4]^+ + CH_4$
5. $M + R^+ \rightarrow M^+ + R^\circ$	Charge transfer	$C_4H_6 + NO^+ \rightarrow C_4H_6^+ + NO$
6. $M + R^+ \rightarrow M^+ + MH^\circ + (R-H)^\circ$	Dissociative charge transfer	$C_{14}H_8Cl_4$(DDE) $+ CH_5^+ \rightarrow C_{14}H_8Cl_3^+ + HCl + CH_4$
7. $M + e^- \rightarrow M^-$	Electron attachment	$C_7H_6O + e^- \rightarrow C_7H_6O^-$
8. $M + e^- \rightarrow M^- + M^\circ$	Dissociative electron attachment	$H_2O + e^- \rightarrow H^- + OH$

M = un-ionized molecules, M^+ and M° = fragment ions or radicals, R^+ and R° = reagent ion or product radical.

The ion beam leaving the focus region passes into the analyzer where it is separated so as to produce the mass spectrum. There are many ways that a beam can be mass analyzed; however, the most commonly used approaches in environmental analyses utilize either the quadrupole principle or some form of magnetic deflection.

The quadrupole analyzer consists of four parallel conducting rods that are positioned to form a quadrant as shown in Fig. 10. Mass selection is achieved by causing ions drifting in the quadrupole region to oscillate in such a way that all ions other than those desired will be electrically neutralized before reaching the detector. Functionally, this is done by superimposing a radio-frequency (rf) voltage on the dc potential existing between adjacent rods. Mass selection is based on solutions to the equations that govern trajectory of ions in quadrupole fields (Matheiu function). Properties of the solutions to these equations have been discussed in detail for quadrupole mass spectrometers by Dawson and Whetten [31].

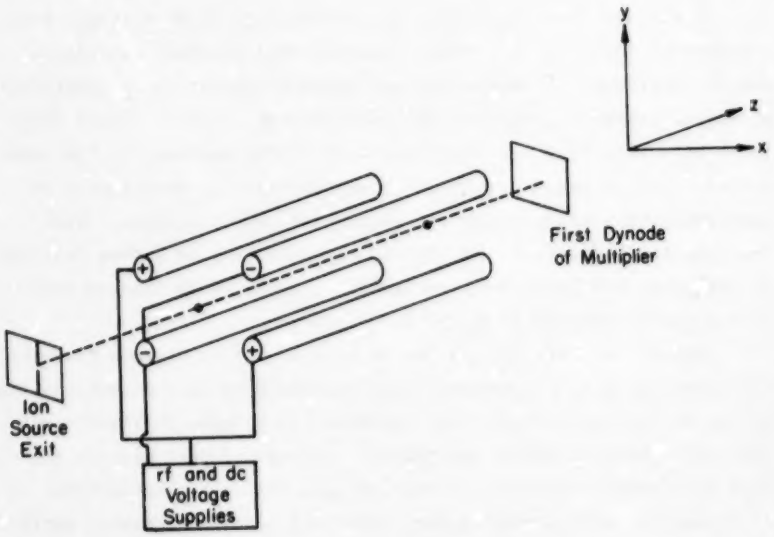

Figure 10. Quadrupole structure showing associated axes.

The magnetic deflection analyzer makes use of the deflection of a charged particle in a magnetic field to provide mass analysis. Scanning of either the ion accelerating voltage or the magnetic field will produce a mass spectrum. Both methods have been used by instrument manufacturers. Magnetic scanning is preferred because voltage scanning produces greater mass discrimination, a change in ion momentum that results in low sensitivity for high-mass ions.

V. COMPUTER INTEGRATION

The combination of gas chromatography and mass spectrometry provides a very useful tool for identification of organic pollutants in water; however, it is labor intensive if data acquisition, reduction, and interpretation are all done manually. Modern instruments can be interfaced to dedicated computers to provide computer control of data acquisition as well as computerized data reduction. A computer-controlled system is not only much faster than a manual system but is also free of errors caused by operator carelessness.

To evaluate the application of computerized GC-MS systems to environmental analysis, the Athens Environmental Research Laboratory and the Environmental Monitoring and Support Laboratory in Cincinnati purchased identical computerized GC-MS systems in 1971. Since that time, more than 20 EPA laboratories have chosen essentially the same system. A minicomputer in this system controls the operation of a quadrupole mass spectrometer and associated output devices. With the computerized system, the applied time required to gather data and prepare them for interpretation was decreased by more than an order of magnitude compared to manual GC-MS systems.

Digital computer control can be applied easily because the mass-to-charge ratio of a quadrupole mass spectrometer is a direct function of the associated voltage. The computer can be mass calibrated automatically before a sample run begins. During the run, digital signals from the computer control the rod voltages for each mass desired.

Changing of voltages is very rapid and therefore permits rapid scanning of all or selected parts of the spectrum. Typically, scan

times between 2 and 20 ms per unit mass are used. As may be seen in the comparison of weak spectra of 1,1-dichloro-1,2-dibromoethane in Fig. 11a and b, slower scanning produces spectra that approach the theoretical ratio (Fig. 11c) of peak intensities (that is, the theoretical ratio of peaks based on the natural abundances of H, D, ^{12}C, ^{13}C, ^{35}Cl, ^{37}Cl, ^{79}Br, and ^{81}Br) better than does rapid scanning. This difference is caused by the fact that too few ions arrive at the detector for acceptable ion statistics when fast scans are used.

An important advantage of quadrupole instruments over magnetic instruments follows from the fact that computer-controlled voltage changes are rapid. It takes no more time to switch from monitoring

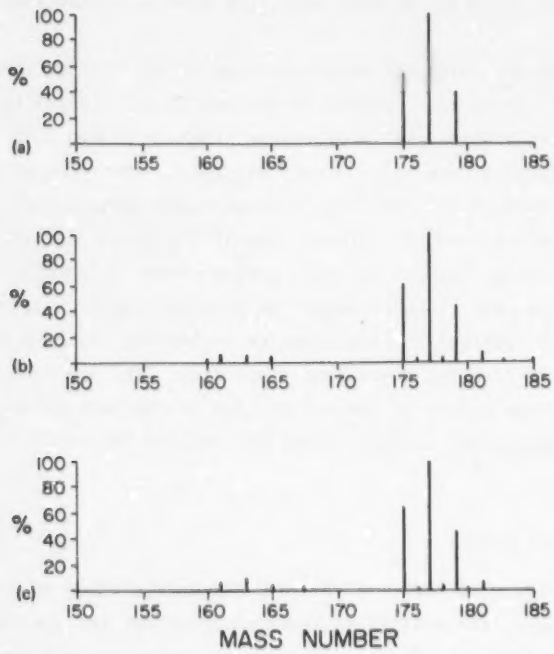

Figure 11. Mass spectra of primary fragment region of 1,1-dichloro-1,2-dibromoethane: (a) 1-msec/amu scan; (b) 17-msec/amu scan; (c) theoretical peak ratios.

mass 500 than it does to switch from mass 37 to mass 38. This selectivity permits the use of specific ion monitoring [32,33] as a tool for sensitive detection of suspected pollutants present at trace levels. Polychlorinated biphenyls, for example, are complex mixtures present at low levels in some environmental samples. Instead of scanning a full mass range from m/e 35 to m/e 450, the molecular ion cluster (caused by the fact that the ions contain both ^{35}Cl and ^{37}Cl isotopes) for trichlorobiphenyls at m/e 256-262 and tetrachlorobiphenyls at m/e 290-298 can be monitored. For scans of equal total times, the mass spectrometer has about 30 times longer to collect signals from each specific ion monitored than for the full mass scan. Therefore, the signal-to-noise ratio increases by a factor of about 6. This means that the monitoring technique is more sensitive than is conventional scanning.

In addition to operating the mass spectrometer and storing the data, the computer can be very helpful in processing and displaying the data. The reconstructed gas chromatogram given in Figure 2 is an example. The computer can also be very helpful in obtaining accurate mass spectra through the technique of background subtraction. The mass spectra of a GC peak of interest may also contain signals from ions of co-eluting residual solvent, column bleed, or an adjacent poorly resolved peak. The operator can select a nearby spectrum that consists almost entirely of the unwanted background and have the computer subtract it from the contaminated spectrum. The spectrum given in Fig. 1 is the result of the subtraction of the background represented by spectrum 102 of Fig. 1 from the peak of interest, spectrum 103.

VI. SPECTRA INTERPRETATION

When the mass spectra have been recorded and the data reduced to provide suitable outputs, the analyst is ready to interpret the spectra and to identify pollutants. Three complementary approaches are used in spectral interpretation. The first of these requires a detailed knowledge of fragmentation processes of charged organic molecules on

the part of the analyst and is beyond the scope of this chapter. McLafferty has summarized the steps to observe in this approach [34]. The second approach, which is widely used by itself and as an adjunct to the other methods, is manual peak matching of unknown spectra against printed reference collections of spectra. The third approach is to use a digital computer to assist in the identification.

Manual peak matching involves comparing the intensity for several spectral peaks, usually about eight of the most abundant, with those of literature spectra. Sorted lists such as those of the Mass Spectral Data Centre [35] and of Cornu and Massot [36] give the fastest manual search results for a small number of unknowns; use of the same lists for large numbers of unknown is tedious and relatively slow.

Computerized spectra matching is a practical and rapid way to obtain a probable identification of unknowns. Within EPA, when a spectrum such as that of Fig. 1 is prepared for spectral matching [37], it is first computer abbreviated based on the Biemann [38] process: the spectrum is split into 14-mass unit groupings, and only the two most intense mass peaks are retained from each group. This computer abbreviation step for the example spectrum shown in Fig. 1 results in the following digitalized data:

Mass	Relative intensity (%)
39	5.1
43	5.0
51	3.0
57	3.2
63	5.3
65	10.4
89	4.8
91	100.0
92	64.5

In EPA GC-MS laboratories, the digitized, abbreviated spectrum can be transferred automatically by a dedicated minicomputer from a remote laboratory to a central computer for spectra matching.

Computer matching includes many approaches, all of which require a large library of reference spectra for best performance. The following are some of the more common approaches:

The five most intense peaks in the spectrum are compared with the five most intense peaks in each spectrum of a reference file. The method is very fast but is not very selective.

The Biemann abbreviation of the unknown and reference spectra are compared on a "peak-no-peak" basis. This program is very rapid on a disk-based computer. It is satisfactory for many files of less than a thousand spectra, but it is not sufficiently selective for larger files.

The Mass Spectral Search System [39] is a collection of programs to identify spectra based on automatic spectra matching or interactive sequential screening of a reference data base containing spectra of more than 35,000 compounds. This collection of programs is presently the most widely used spectra-matching system available on a central computer.

Probability-based matching [40] examines the complete unknown spectrum for ions that are significant in spectra from the reference library. This rapid, reverse-search method can correctly identify the major components of mixtures.

When the reference spectra data base does not include a spectrum of the unknown, straightforward matching cannot provide a correct identification. To help the analyst in such situations, several learning machine approaches have been developed. The best known of these are the DENDRAL (dendritic algorithm) program [41] and the STIRS (self-training interpretive and retrieval system [42]. Each deduces structural information based on the unknown mass spectrum and the molecular weight of the unknown. The DENDRAL program also prepares a listing of structures that are compatible with the input spectrum. STIRS summarizes all substructures that are present in the unknown and lists the probability for each.

Regardless of whether the spectral identification is done by one versed in fragmentation processes, manual spectra matching, or computerized interpretation, the final step in GC-MS-computer pollutant identification is confirmation of the identification. All identifications should be considered tentative, at least until the relative GC retention time and the electron-impact cracking pattern of the unknown are found to match those of an authentic standard. For greater confidence, the confirmation process should include other types of spectral comparisons such as chemical ionization cracking patterns, high-resolution cracking patterns, or infrared spectra.

Many organic pollutant identifications have been made in water since this work began in 1968 [43,44]. Based on a recent compilation of more than 1300 compounds that have been identified in waters of all types [45], the 10 most frequently identified organic compounds are chloroform, methylene chloride, bromodichloromethane, toluene, chlorodibromoethane, tetrachloroethylene, naphthalene, benzene, carbon tetrachloride, and phenol. Much of the success in identifying trace levels of organics can be attributed to improvements in analytical techniques involving gas chromatography-mass spectrometry. Although there may never be a single universal sampling, separation, and analytical method suitable for all organic water pollutants, GC-MS at present best meets the environmental analytical chemist's requirements.

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